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MARCH 1955

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PREPARED UNDER
CONTRACT NO. DA-18-064-CML-2518
CHEMICAL CORPS, U. S. ARMY

IMM-NYU 215
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This report represents results obtained at the Institute of Mathematical Sciences, New York University, under the auspices of the United States Army Chemical Corps, Contract No. DA-18-064-CML-2518.

Growth of Drops by Condensation

by

Ignace I. Kolodner

When the vapor pressure (or concentration) in air surrounding a liquid nucleus exceeds the saturation pressure for a given temperature, vapor will condense on the nucleus and the drop will grow. The object of this report is to determine this growth. The problem, although of great interest in itself, is preliminary to the much more difficult study of behavior of a collection of drops in supersaturated medium -- a situation which may serve as a model of the formation of clouds.

In Section I the problem is formulated. Section II contains the discussion of results obtained here in comparison with certain results already available. The remainder of the paper is devoted to derivations and proofs. Many proofs are merely sketched.

I. Formulation

In order to determine the radius $R(t)$ of the drop it is necessary to consider simultaneously the concentration of vapor $c(r,t)$ around the drop. If we assume that the temperature remains constant and the drop remains spherical, then $c(r,t)$ and $R(t)$ can be determined by solving the following problem:

$$
(1)\quad \begin{cases}
\text{DE} & c_{rr} + \frac{2}{r} c_r = c_t \quad \text{for} \quad r > R(t), \quad t > 0 \\
\text{Bc1} & c(R(t),t) = 1 \quad \text{for} \quad t \geq 0 \\
\text{Bc2} & a c_r(R(t),t) = \mathring{R}(t) \quad \text{for} \quad t > 0 \\
\text{Ic} & c(r,0) = 0 \quad \text{for} \quad r > 1 \\
\infty\text{c} & c(\infty, t) = 0 \quad \text{for} \quad t \geq 0 \\
\text{Ic} & R(0) = 1.
\end{cases}
$$

In equations (1) all quantities are in the dimensionless form given in [1] (see equations (7) - (12) in [1]). The connection between these and the actual variables $\bar{r}$, $\bar{t}$ and concentration $\bar{c}$ is given by:

$$
(2)\quad \begin{aligned}
\bar{r} &= ar \\
\bar{t} &= \frac{a^2}{D} t \\
\bar{c}(\bar{r},\bar{t}) &= (g - c_o)c(r,t) + c_o
\end{aligned}
$$

while

$$
(3)\quad a = \frac{g - c_o}{\rho - g} .
$$

The meaning of symbols used is:

a - initial radius of the liquid nucleus

D - coefficient of diffusion

ρ - density of liquid

$g = g(T)$ - saturation concentration at a given temperature

c_o - initial concentration of the liquid's vapor.

In the problem under consideration, $g < c_o$, hence $\alpha < 0$. On the other hand, since $\rho > c_o$, $\alpha = -\frac{c_o - g}{\rho - g} > -1$, while $\alpha = -1$ only when $\rho = c_o$, that is, under critical conditions, in which case liquid cannot be distinguished from vapor. (As it turns out, the mathematical problem as posed has no solution for $\alpha \leq -1$ in accordance with the fact that no physical situation leads to such values for α.) For water droplet in air, at 73^oF, $g = 2 \times 10^{-5}$ g/cm^3; hence, assuming that the initial concentration is twice the saturation concentration, $\alpha = -2 \times 10^{-5}$. In general, α is expected to be of this order of magnitude.

II. Review of results

While the corresponding one-dimensional problem can be solved explicitly, only approximate and hardly justifiable attacks were known to apply in the three-dimensional case. The simplest among these is the so-called quasistatic approach which uses the assumption that $c(r,t)$ is slowly varying in time. The term c_t is then dropped from the differential equation, thus forcing a solution of the form

$$c(r,t) = f(t)r^{-1} + g(t). \tag{4}$$

From the condition at infinity we then get that $g(t) \equiv 0$, while the first boundary condition determines

$$f(t) = R(t). \tag{5}$$

On substituting in the second boundary condition, we now get

$$(6) \qquad \overset{\circ}{R} = -\alpha R^{-1}$$

or, on integrating,

$$(7) \qquad R^2 = 1 - 2\alpha t.$$

In this method, the initial condition on c is violated.

A second type of attack which is in fashion with physical chemists, consists in assuming that the boundary moves slowly, so that it could be at first considered that $\overset{\circ}{R} = 0$. (This is equivalent to the assumption that α is small and the method ought to lead to the beginning of an expansion of the solution in powers of α). Then $R = 1$, and the system (1) less the second boundary condition is solved with $R = 1$, and the result is used to get an improved equation for $R(t)$ by using the second boundary condition. Thus we get

$$(8) \qquad c(r,t) = \frac{2}{r\sqrt{\pi}} \int_{\frac{r-1}{2\sqrt{t}}}^{\infty} e^{-\sigma^2},$$

from which

$$(9) \quad c_r(r,t) = -\frac{2}{r\sqrt{\pi}}\left(\frac{1}{r}\int_{\frac{r-1}{2\sqrt{t}}}^{\infty} e^{-\sigma^2}\,d\sigma + \frac{1}{2\sqrt{t}}\, e^{-\left(\frac{r-1}{2\sqrt{t}}\right)^2}\right).$$

If we set in (9) $r = R = 1$, and then use 1 - Bc2, we will get a result too much at variance with the quasistatic solution

(7), namely,

$$(10) \qquad R = 1 - at - \frac{2a}{\sqrt{\pi}}\sqrt{t} \ .$$

If on the other hand, one does not specify R in (9), one gets on using $1 - Bc2$ a complicated differential equation to solve. Of course one can force an asymptotic agreement with the quasi-static solution by replacing in (9) r by $R(t)$ outside the parenthesis, and by 1 inside. For then one gets, on using the second boundary condition,

$$(11) \qquad R^2 = 1 - 2at - \frac{4a}{\sqrt{\pi}}\sqrt{t} \ .$$

It is usually argued in favor of formula (7) or (11) on the basis that experimental data predict a linear growth of the area ($4\pi R^2$) of the droplet. But this by no means insures that the mathematical theory is sufficiently correct for purpose of prediction, since the available experimental data need not cover a sufficiently large parameter range, while the mathematical validity of these formulae is doubtful. (They were, indeed, almost forced into agreement with an experimental formula).

Another deficiency of the methods just discussed is that they are difficult to iterate to get even formal corrections. A better, although still formal attack has been devised in [1], where formula (11) was arrived at, accompanied by a statement

that the error is of order of $\sqrt{\alpha}$.

In this paper the problem is solved rigorously. Although complicated and powerful techniques had to be used, we get a simple practical result. We find that for $\beta = -\alpha$ sufficiently small, there are three numbers, A, B, and $k > 1$ such that for <u>all</u> t,

$$(12) \qquad \begin{cases} A + \dfrac{B}{\sqrt{t}} \leq R\dot{R} \leq k(A + \dfrac{B}{\sqrt{t}}) \\ \\ 1 + 2At + 4B\sqrt{t} \leq R^2 \leq 1 + k(2At + 4B\sqrt{t}). \end{cases}$$

Thus, both $R\dot{R}$ and R^2 are determined for all t within the relative error of $(k - 1)$. For $\beta \leq .05$, a crude estimate for the constants is given by

$$(13) \qquad \begin{cases} A = \beta = -\alpha \\ B = \dfrac{\beta}{\sqrt{\pi}} e^{-\beta} \\ k = 1 + 4.32\sqrt{\beta}. \end{cases}$$

For the case specified in Section I, formula (13) gives $k = 1.0122$, showing that formula (12) determines the radius with a relative error of .0122.

As already stated, formula (13) gives only a crude estimate. In Section V we discuss a simple numerical procedure of obtaining sharper estimates. Thus in the case considered ($\beta = 2 \times 10^{-5}$) one can show that while A and B can still be taken as determined by (13), k is reduced to 1.00563. For

larger β, however, say $\beta = .05$, while (13) yields

$$A = .05$$
$$B = .0267$$
$$k = 1.96$$

the method discussed in Section V leads to a sharper result,

$$A = .05254 = 1.051\ \beta$$
$$B = .0281 = 1.052\ \frac{\beta}{\sqrt{\pi}}\ e^{-\beta}$$
$$k = 1.338.$$

Incidentally, these considerations show that formula (11) is, after all, quite satisfactory, and that the assumed mathematical model for condensation predicts a linear growth of area of the drop. While a correct asymptotic behavior is predicted the deviation of the approximate result from the actual solution may be considerable for $\beta \geq .05$.

III. Condensation problem vs. evaporation problem

The evaporation problem discussed by the author in [2] is formally identical with the condensation problem, see [2], p. 1, the only difference being that in the former $\alpha > 0$, while now $-1 < \alpha < 0$. This seemingly small difference is sufficiently important, however, to invalidate the main results of [2].

Let us briefly review the method used in solving the evaporation problem. We first constructed an auxiliary function,

eq. [2]-(18),

$$(14) \qquad u^{\rho}(r,t) = \frac{1}{2}\int_0^t \frac{\rho(\sigma)}{t-\sigma}\, z - \frac{(1+a^{-1})\rho(\sigma)\dot{\rho}(\sigma)+1}{\sqrt{t-\sigma}}\,\eta(z)\,d\sigma,$$

defined for $-\infty < r < \infty$, $t > 0$, $r \neq \rho(t)$, where

$$(15) \qquad z = z(r,\sigma) = \frac{r-\rho(\sigma)}{2\sqrt{t-\sigma}}$$

$$(16) \qquad \eta(z) = \frac{1}{\sqrt{\pi}}\exp(-z^2),$$

while $\rho(t)$ was an arbitrary function. If $\rho(t)$ were the actual evaporation curve, equation (14) would yield $rc(r,t)$ for $r \geq \rho(t)$, and would be identically zero for $r < \rho(t)$. We next observed that if $R(t)$ is the solution of

$$(17) \qquad u_r^{\rho}(\rho^-,t) = 0, \qquad \rho(0) = 1,$$

and if in addition $\dot{R} < 0$, then

$$(18) \qquad u^R(r,t) \equiv 0 \quad \text{for} \quad r < R(t), \quad \text{(theorem [2]-3)},$$

and as a consequence, $u^R(r,t)$ for $r > R(t)$ satisfies all the conditions required of $rc(r,t)$, (main theorem), concluding that $\frac{1}{r}u^R(r,t)$ is the concentration and $R(t)$ is the evaporation curve. Thus the whole problem was reduced to solving equation (17), and showing that its solution $R(t)$ has the property $\dot{R}(t) < 0$.

If now we would proceed in the same manner in the condensation case, it would still follow that equation (17) has a (unique) solution $R(t)$, but that $\dot{R} > 0$. Because of this

theorem [2]-3, although actually true, could not be proven to be a consequence of (17).

The difficulty is circumvented as follows. Let $\bar{R}(t)$ be the solution of

$$(19) \qquad u_r^{\rho}(\rho^-,t) + \frac{1}{2}\dot{\rho}u^{\rho}(\rho^-,t) = 0, \qquad \rho(0) = 1.$$

Explicitly, this equation is

$$(19)' \begin{cases} \rho\overset{\circ}{\rho} = -2\alpha\left[\int_{-\infty}^{z(\rho,0)} \eta(\tau)d\tau + \frac{1}{2\sqrt{t}}\,\eta(z(\rho,0))\right] \\ \quad + \int_0^t \frac{\rho(\sigma)\dot{\rho}(\sigma)}{t-\sigma}\, z(\rho,\sigma)\,\eta(z(\rho,\sigma))d\sigma \\ \quad - \alpha\left[\rho\overset{\circ}{\rho}\int_{-\infty}^{z(\rho,o)} \eta(\tau)d\tau + \dot{\rho}\sqrt{t}\,\eta(z(\rho,o))\right] \\ \quad - \dot{\rho}\int_0^t \frac{\rho(\sigma)\dot{\rho}(\sigma)}{\sqrt{t-\sigma}}\,\eta(z(\rho,\sigma))d\sigma \end{cases}$$

$$\rho(0) = 1$$

(wherever ρ appears without argument, the argument is meant to be t).

We assert:

<u>Theorem 1</u>. Equation (19) has a unique solution $\bar{R}(t)$.

<u>Theorem 2</u>. $u^{\bar{R}}(r,t) \equiv 0$ for $r < \bar{R}(t)$, $t > 0$.

<u>Main theorem</u>. $c(r,t) = \frac{1}{r}\,u^{\bar{R}}(r,t)$ for $r > \bar{R}(t)$ satisfies all conditions (1).

We omit the proof of theorem 1. It is observed that in view of theorem 2,

$$u_r^{\bar{R}}(r,t) = 0 \qquad \text{for} \quad r < \bar{R}(t),$$

hence, as r approaches $\bar{R}(t)$ from the left,

$$u_r^{\bar{R}}(\bar{R}^-,t) = 0.$$

Thus $\bar{R}$, after all, satisfies equation (17), and since this equation, as is shown in Section IV, has a unique solution $R(t)$, $\bar{R}(t) \equiv R(t)$, and therefore $\bar{R}(t)$ could be determined by solving (17) instead of (19). Yet we were unable to prove that the converse is implied. This is explained in more detail in the Appendix where the proof of theorem 2 is established. The proof of the main theorem is the same as in [2], p. 9.

IV. Determination of the condensation curve: Theoretical considerations.

We observed already that $R(t)$ is the solution of equation (17), and we shall use this equation to study the behavior of $R(t)$ in preference to the defining equation (19). Equation (19) differs from (17) by an extra term, $\frac{1}{2}\,\dot{\rho}u^{\rho}(\rho^-,t)$, which will vanish if ρ is replaced by the solution $R(t)$. Explicitly, equation (17) is

$$\text{(20)} \qquad \begin{cases} \rho\dot{\rho} = G(\rho) \\ \rho(0) = 1 \end{cases}$$

where

$$(21)\qquad G(\rho) = -2\alpha\left[\int_{-\infty}^{z(\rho,0)} \eta(\tau)d\tau + \frac{1}{2\sqrt{t}}\,\eta(z(\rho,0))\right]$$
$$+\int_0^t \frac{\rho(\sigma)\dot{\rho}(\sigma)}{t-\sigma}\, z(\rho,\sigma)\,\eta(z(\rho,\sigma))d\sigma.$$

It is the same equation as in the case of evaporation, yet because of different sign of α, the method used in [2] to produce the solution and its approximations does not apply here.

As is well known (and easily verified), the solution will have a derivative behaving as $t^{-1/2}$ near $t = 0$. This suggests that we introduce $x = \sqrt{t}$ as the independent variable. To preserve the form of the second integral we also introduce $s = \sqrt{\sigma}$ as a new integration variable. Let $y(x) = y(\sqrt{t}) = \rho(t)$. Equation (20) is then transformed into an equation for y,

$$(22)\qquad \begin{cases} yy' = H(y) \\ y(0) = 1 \end{cases}$$

where

$$(23)\qquad H(y) = 2xG(\rho) = 2\beta\left[2x\int_{-\infty}^{z(y,0)} \eta(\tau)d\tau + \eta(z(y,0))\right.$$
$$\left. + 2x\int_0^x \frac{y(s)y'(s)}{x^2 - s^2}\, z(y,s)\,\eta(z(y,s))ds\right.$$

$$(24)\qquad z(y,s) = \frac{y(x) - y(s)}{2\sqrt{x^2 - s^2}}, \qquad z(y,0) = \frac{y(x) - 1}{2x}$$

$$(25)\qquad \beta = -\alpha > 0.$$

Our object is primarily to derive upper and lower bounds for the solution. Having this in mind, it is convenient to considêr a transformation $K(u,v)$ on couples of functions $(u(x),v(x))$, defined by

(26) $$K(u,v) = 2\beta\left[2x\int_{-\infty}^{z(u,0)} \eta(\tau)d\tau + \eta(z(v,0))\right] + 2x\int_0^x \frac{u(s)u'(s)}{x^2 - s^2}\,\xi(u,v)\;\eta(\xi(u,v))ds$$

where

(27) $$\xi(u,v) = \frac{1}{2\sqrt{x^2 - s^2}}\int_s^x \frac{u(\sigma)u'(\sigma)}{v(\sigma)}\,d\sigma \;.$$

It is observed that if $u = v$, then, since $\xi(u,u) = z(u,s)$, $K(u,u) = H(u)$. We shall now assume the existence of two differentiable functions u_o, v_o having the properties:

(28) $$\begin{cases} u_o(0) = 1, \quad v_o(0) = 1, \; 0 < u_o u_o' \leq v_o v_o', \quad \text{for all } x \geq 0 \\ \dfrac{v_o v_o'}{u_o} \leq \sqrt{2} \\ u_o u_o' \leq K(u_o,v_o) \\ v_o v_o' \geq K(v_o,u_o) \end{cases}$$

These functions will be constructed explicitly in the next section. As to functions u,v, on which $K(u,v)$ applies we shall require that

(29) $$u(0) = 1, \qquad u_o u_o' \leq uu' \leq v_o v_o' \;.$$

Such functions will be said to belong to class $\mathcal{K}$.

Theorem 1. Let $u, \bar{u}, v, \bar{v} \in \mathcal{K}$, and let furthermore

$$uu' \leq \overline{uu'}, \quad vv' \geq \overline{vv'}, \quad \text{for all} \quad x \geq 0.$$

Then

$$K(u,v) \leq K(\bar{u},\bar{v}), \qquad x \geq 0.$$

Proof: 1) $z(u,0) \leq z(\bar{u},0)$ since $u \leq \bar{u}$,

hence $\int_{-\infty}^{z(u,0)} \eta(\tau)d\tau \leq \int_{-\infty}^{z(v,0)} \eta(\tau)d\tau$

2) $z(v,0) \geq z(\bar{v},0)$ since $v \geq \bar{v}$,

hence $z^2(v,0) \geq z(\bar{v},0)$, since $u > 0$, $v > 0$;

consequently $\eta(z(v,0)) \leq \eta(z(\bar{v},0))$

3) $0 < \dfrac{u(\sigma)u'(\sigma)}{v(\sigma)} \leq \dfrac{\bar{u}(\sigma)\bar{u}'(\sigma)}{\bar{v}(\tau)}$;

furthermore $\dfrac{\bar{u}(\sigma)\bar{u}'(\sigma)}{\bar{v}(\sigma)} \leq \dfrac{v_o(\sigma)v_o'(\sigma)}{u_o(\sigma)} \leq \sqrt{2}$,

hence $0 < \xi(u,v) \leq \xi(\bar{u},\bar{v}) \leq \frac{1}{\sqrt{2}}\sqrt{\frac{x-s}{x+s}} \leq \frac{1}{\sqrt{2}}$. But $z\eta(z)$ $= \frac{z}{\sqrt{\pi}} \exp(-z^2)$ is an increasing function of z for $0 \leq z \leq \frac{1}{\sqrt{2}}$; hence, $\xi(u,v)\eta(\xi(u,v)) \leq \xi(\bar{u},\bar{v})\eta(\xi(\bar{u},\bar{v}))$. Since also $u(s)u'(s) \leq \bar{u}(s)\bar{u}'(s)$, it follows that

$$\int_0^x \frac{u(s)u'(s)}{x^2 - s^2} \xi(u,v)\eta(\xi(u,v))ds \leq \int_0^x \frac{\bar{u}(s)\bar{u}(s)}{x^2 - s^2} \xi(\bar{u},\bar{v})\eta(\xi(\bar{u},\bar{v}))ds.$$

The proof is completed on adding the three inequalities.

Theorem 2. Let the sequences u_n, v_n be recursively defined by

$$\begin{cases} u_n(0) = v_n(0) = 1 \\ u_n u_n' = K(u_{n-1}, v_{n-1}), \quad v_n v_n' = K(v_{n-1}, u_{n-1}). \end{cases}$$

Then:

1) u_n is a monotonically increasing sequence and converges to a function $\tilde{u}$,
2) v_n is a monotonically decreasing sequence and converges to a function $\tilde{v}$,
3) $\tilde{u}\tilde{u}' \leq \tilde{v}\tilde{v}'$ for all $x \geq 0$,
4) $\tilde{u}\tilde{u}' = K(\tilde{u},\tilde{v})$, $\tilde{v}\tilde{v}' = K(\tilde{v},\tilde{u})$.

Proof of this theorem is implied in [3].

Theorem 3. Let $u, v, \bar{u}, \bar{v} \in \mathcal{K}$, and furthermore assume that $u \equiv v$ for $x \leq a$, $a \geq 0$. Then there exist two numbers, $\Delta > 0$ and $0 \leq \lambda < 1$ such that for $x \leq a + \Delta$,

$$|K(u,v) - K(\bar{u},\bar{v})| \leq \frac{1}{2}\lambda\left(\underset{0\leq x\leq a+\Delta}{\text{l.u.b.}} |uu' - \overline{uu}'| + \underset{0\leq x\leq a+\Delta}{\text{l.u.b.}} |vv' - \overline{vv}'| \right) .$$

This theorem asserts essentially that $K(u,v)$ satisfies a "Lipschitz Condition". We omit the proof which is tedious but not difficult.

Corollary 1. $\tilde{u} \equiv \tilde{v}$.

Proof: $\tilde{u}(0) = \tilde{v}(0) = 1$. Suppose that it has been established that $\tilde{u} \equiv \tilde{v}$ for $x \leq a$, but $\tilde{u} \not\equiv \tilde{v}$ for $x \geq a$. But then, in view of Theorems 2 and 3,

$$|\tilde{u}\tilde{u}' - \tilde{v}\tilde{v}'| = |K(\tilde{u},\tilde{v}) - K(\tilde{v},\tilde{u})| \leq \lambda \underset{0 \leq x \leq a+\Delta}{\text{l.u.b.}} |\tilde{u}\tilde{u}' - \tilde{v}\tilde{v}'|.$$

Hence,

$$\underset{0 \leq x \leq a+\Delta}{\text{l.u.b.}} |\tilde{u}\tilde{u}' - \tilde{v}\tilde{v}'| \leq \lambda \underset{0 \leq x \leq a+\Delta}{\text{l.u.b.}} |\tilde{u}\tilde{u}' - \tilde{v}\tilde{v}'|,$$

and since $\lambda < 1$, $\tilde{u}\tilde{u}' \equiv \tilde{v}\tilde{v}'$ for $0 \leq x \leq a+\Delta$, or $\tilde{u} \equiv \tilde{v}$ for $0 \leq x \leq a+\Delta$. Since a is any number, it follows that $\tilde{u} \equiv \tilde{v}$ for all x.

Corollary 2. Equation (22) has a unique solution y and $y = \tilde{u} = \tilde{v}$.

Proof: From corollary 1 and theorem 2, $\tilde{u}$ satisfies

$$\tilde{u}\tilde{u}' = K(\tilde{u},\tilde{u}) = H(y).$$

The uniqueness of y is demonstrated similarly as Corollary 1, on observing that $H(y)$ satisfies, by theorem 3, a Lipschitz Condition.

Thus the existence and construction of the solution of equation (22) for the condensation curve is established. While we never doubted that this solution exists, the practical importance of the above consideration lies in that the sequences u_n and v_n defined in theorem 2 form ever improving lower and upper bounds for the solution. Still there is a difficulty

in that while the first iterates are chosen as simple expressions, the successive iterates are usually difficult to compute. This is remedied by the following

<u>Theorem 4</u>. Let $\bar{u}_o, \bar{v}_o \in \mathcal{K}$, such that

$$u_o u_o' \leq \bar{u}_o \bar{u}_o' \leq K(u_o, v_o) \leq K(v_o, u_o) \leq \bar{v}_o \bar{v}_o' \leq v_o v_o' .$$

Then

$$u_o u_o' \leq \bar{u}_o \bar{u}_o' \leq K(\bar{u}_o, \bar{v}_o) \leq K(\bar{v}_o, \bar{u}_o) \leq \bar{v}_o \bar{v}_o' \leq v_o v_o' .$$

<u>Proof</u>: In view of the premises and theorem 1,

$$K(u_o, v_o) \leq K(\bar{u}_o, \bar{v}_o)$$

$$K(v_o, u_o) \geq K(\bar{v}_o, \bar{u}_o)$$

$$K(\bar{u}_o, \bar{v}_o) \leq K(\bar{v}_o, \bar{u}_o),$$

completing the proof.

Thus, in view of theorem 4, the functions $\bar{u}_o$, $\bar{v}_o$ satisfy all the conditions imposed on u_o and v_o, and hence may be used to start a new iteration sequence $\bar{u}_n, \bar{v}_n$, which will have the same properties as the sequence u_n, v_n of theorem 2. Of course, rather than to construct such a sequence, we shall reapply theorem 4, to get improved lower and upper bound of a certain form. Such a procedure will not, of course, lead to an exact result, but, as we shall see, the improvement may be considerable.

V. Determination of condensation curve: Calculation of Bounds.

In view of the form of $K(u,v)$, eq. (26), it is reasonable to conjecture the existence of bounds u_o^2, v_o^2 which are quadratic in x. We thus assume that u_o, v_o can be chosen as

$$(30) \qquad \begin{cases} u_o u_o' = ax + b & u_o(0) = 1 \\ v_o v_o' = k(ax + b) & v_o(0) = 1. \end{cases}$$

Our object is to establish this conjecture, i.e. to show that with appropriate values for a, b, and k, conditions (28) are satisfied, and to determine the best such values. For the latter purpose we use the theorem 4 of the preceding section.

Let us first study functions of the form

$$w = \sqrt{1 + px^2 + 2qx}\,, \qquad p, q > 0, \quad p > q^2.$$

We have:

$$z(w,0) = \frac{w-1}{2x}\,, \quad z' = \frac{1}{2x^2}(xw' - w + 1); \ (xw' - w + 1)' = xw''$$

$$(ww')' = ww'' + w'^2 = ww'' + \frac{(ww')^2}{w^2} = p.$$

Hence

$$w^3 w'' = pw^2 - (ww')^2 = p(1 + px^2 + 2qx) - (px + q)^2 = p - q^2.$$

Thus, if $p > \sqrt{q}$, $w'' > 0$, w' is increasing, $xw' - w + 1$ is increasing and thus positive, so that z' is positive, and so z is increasing. We therefore have

$$\frac{q}{2} = z(w(0),0) < z < z(w(\infty),0) = \frac{\sqrt{p}}{2}$$

$$q = w'(0) < w' < w'(\infty) = \sqrt{p} \; .$$

Applying this to u_o and v_o which have the same form as w, we get

$$(31) \quad \begin{cases} \frac{b}{2} \leq z(u_o,0) \leq \frac{\sqrt{a}}{2} \\ \frac{kb}{2} \leq z(v_o,0) \leq \frac{\sqrt{ka}}{2} \\ b \leq \frac{u_o u_o'}{v_o} = \frac{ax + b}{\sqrt{1 + k(ax^2+2bx)}} = \frac{v_o'}{k} \leq \sqrt{\frac{a}{k}} \\ kb \leq \frac{v_o v_o'}{u_o} = \frac{k(ax + b)}{\sqrt{1 + ax^2 + 2bx}} = ku_o' \leq k\sqrt{a} \\ \frac{b}{2}\sqrt{\frac{x - s}{x + s}} \leq \zeta(u_o,v_o) \leq \frac{1}{2}\sqrt{\frac{a}{k}}\sqrt{\frac{x - s}{x + s}} \\ \frac{kb}{2}\sqrt{\frac{x - s}{x + s}} \leq \zeta(v_o,u_o) \leq \frac{k\sqrt{a}}{2}\sqrt{\frac{x - s}{x + s}} \; . \end{cases}$$

We assume that

$$(32) \qquad b < \sqrt{\frac{a}{k}} \, , \quad k\sqrt{a} \leq \sqrt{2} \; .$$

The first of these is imposed by the condition $p > \sqrt{q}$ (and it is anticipated that this will be met in our case), while the second is required by one of the conditions (28).

We now have, using the definition of $K(u,v)$, and (31)

$$
(33)\quad\begin{cases}
K(u_o, v_o) \geq 2\beta x(1 + \operatorname{erf}(\frac{b}{2})) + \frac{2\beta}{\sqrt{\pi}} \exp(-\frac{ka}{4}) \\
\quad + \frac{2x}{\sqrt{\pi}} \int_0^x \frac{as + b}{x^2 - s^2} (\frac{b}{2}\sqrt{\frac{x - s}{x + s}}) \exp(-(\frac{b}{2}\sqrt{\frac{x - s}{x + s}})^2) ds \\
\quad = L(a, b, k, x) \\
K(v_o, u_o) \leq 2\beta x(1 + \operatorname{erf}(\frac{\sqrt{ka}}{2})) + \frac{2\beta}{\sqrt{\pi}} \exp(-\frac{b^2}{4}) \\
\quad + \frac{2x}{\sqrt{\pi}} \int_0^x \frac{k(as + b)}{x^2 - s^2} \left(\frac{k\sqrt{a}}{2}\sqrt{\frac{x - s}{x + s}}\right) \exp(-(\frac{k\sqrt{a}}{2}\sqrt{\frac{x - s}{x + s}})^2) ds \\
\quad = U(a, b, k, x).
\end{cases}
$$

If we require that

$$
(34)\quad\begin{cases}
u_o u_o' \leq L(a, b, k, x) \\
v_o v_o' \geq U(a, b, k, x),
\end{cases}
$$

the conditions imposed on u_o, v_o, equations (28) will be a fortiori satisfied. The integrals in L and U can be evaluated explicitly and one gets,

$$
(35)\quad\begin{cases}
L(a, b, k, x) = \Big\{ 2\beta(1 + \operatorname{erf}(\frac{b}{2})) \\
\qquad + a\Big(\frac{\sqrt{\pi}\, b}{2} [1 - \operatorname{erf}^2(\frac{b}{2})] \exp(+\frac{b^2}{4}) - \operatorname{erf}(\frac{b}{2})\Big)\Big\} x \\
\qquad + \Big\{ \frac{2\beta}{\sqrt{\pi}} \exp(-\frac{ka}{4}) + b \operatorname{erf}(\frac{b}{2}) \Big\} = \underline{a}x + \underline{b} \\
U(a,b,k,x) = \Big\{ 2\beta(1 + \operatorname{erf}(\frac{\sqrt{ka}}{2})) \\
\qquad + ka\Big(\frac{\sqrt{\pi}\, k\sqrt{a}}{2} [1 - \operatorname{erf}^2(\frac{k\sqrt{a}}{2})] \exp(+\frac{k^2 a}{4}) - \operatorname{erf}(\frac{k\sqrt{a}}{2})\Big)\Big\} x \\
\qquad + \Big\{ \frac{2\beta}{\sqrt{\pi}} \exp(-\frac{b^2}{2}) + kb \operatorname{erf}(\frac{k\sqrt{a}}{2}) \Big\} = \bar{a}x + \bar{b}\,.
\end{cases}
$$

Hence, both L and U are linear in x, and inequalities (34) on functions reduce exactly to numerical inequalities,

$$(36)\quad \begin{cases} a \leq \underline{a}(a, b, k) \\ b \leq \underline{b}(a, b, k) \\ ka \geq \overline{a}(a, b, k) \\ kb \geq \overline{b}(a, b, k). \end{cases}$$

It is desirable to solve the inequalities (36) in the best possible way. Since there are only 3 constants to be determined and 4 inequalities to be satisfied, the best we can expect would be 3 equalities and one inequality. Due to complexity of expressions involved this is impossible to achieve explicitly. But a computational procedure to achieve it is available in view of theorem 4 of the preceding section. We first have to find any a_o, b_o, k_o satisfying (36), and then reiterate according to the scheme

$$(37)\quad \begin{cases} a_n = \underline{a}(a_{n-1}, b_{n-1}, k_{n-1}) \\ b_n = \underline{b}(a_{n-1}, b_{n-1}, k_{n-1}) \\ k_n = \max(a_n^{-1}\overline{a}(a_{n-1}, b_{n-1}, k_{n-1}), b_n^{-1}\overline{b}(a_{n-1}, b_{n-1}, k_{n-1})) \end{cases}$$

Theorem (4) then implies that the sequences a_n, b_n are increasing and convergent, and that the sequences k_na_n, k_nb_n are decreasing and convergent. Actually, we do not need to adhere rigidly to the scheme, but may at any step replace any one or two of a_n, b_n, k_n by the same quantities with index lower by unity

to exploit the difference in rapidity with which these sequences may converge.

For the first step we choose,

$$(38)\qquad \begin{cases} a_o = 2\beta \\ b_o = \dfrac{2\beta}{\sqrt{\pi}}\, e^{-\beta} \\ k_o = 2, \end{cases}$$

The first two inequalities of (36) are then obviously satisfied. Using the remaining two inequalities, we get the conditions

$$(39)\qquad \begin{cases} 2 \geq a_o^{-1}\bar{a}(a_o, b_o, 2) \\ 2 \geq b_o^{-1}\bar{b}(a_o, b_o, 2) \end{cases}$$

On observing that for all $p > 0$

$$(40)\qquad \begin{aligned} &\sqrt{\pi}\, p(1 - \operatorname{erf}^2(p))\exp(+p^2) - \operatorname{erf}(p) \\ &= \frac{2}{\sqrt{\pi}}\int_0^x \frac{s}{x^2 - s^2}\left(p\sqrt{\frac{x - s}{x + s}}\right)\exp\left(-p^2\,\frac{x - s}{x + s}\right) ds \\ &\leq \frac{2x}{\sqrt{\pi}}\int_0^x p\sqrt{\frac{x - s}{x + s}}\exp\left(-\,p^2\,\frac{x - s}{x + s}\right)\frac{ds}{x^2 - s^2} = \frac{2}{\sqrt{\pi}}\int_0^p e^{-\sigma^2} d\sigma \leq \frac{2p}{\sqrt{\pi}}\,, \end{aligned}$$

$$\operatorname{erf}(p) \leq \frac{2p}{\sqrt{\pi}}\,,$$

inequalities (39) are satisfied if

$$(41)\qquad \begin{aligned} &2 \geq 1 + 2(1 + 2\sqrt{2})\sqrt{\frac{\beta}{\pi}} \\ &2 \geq e^{\beta} + 4\sqrt{2}\sqrt{\frac{\beta}{\pi}}\,, \end{aligned}$$

that is, if

(41)' $\quad \beta \leq .0508.$

Thus our considerations are restricted to this range of β. Conditions (32) are satisfied if

$$\frac{2\beta}{\sqrt{\pi}} e^{-\beta} \leq \sqrt{2\beta}\ , \quad \text{or} \quad \beta \leq \frac{\pi}{2}$$

$$2\sqrt{2\beta} \leq \sqrt{2}\ , \quad \text{or} \quad \beta \leq .25,$$

hence certainly when β is restricted to the above range. Actually, the range of β for which the method will work is much wider, but we shall not attempt to extend our considerations since the range considered is satisfactory for practical purposes, and since for $\beta = .05$ the relative error in using bounds of the form (30) is already .338 and it will increase with β.

One gets a simple improvement on (38) by iterating (38) once and replacing a_1 by a_o, b_1 by b_o, and using inequalities (40). Thus one gets

(42) $$k_1 = 1 + 2(1 + 2\sqrt{2})\sqrt{\frac{\beta}{\pi}} = 1 + 4.32\sqrt{\beta}\ ,$$

quoted in Section II. Further improvements must be obtained numerically by successive application of (37). We consider three cases, $\beta = .00002$, $\beta = .02$, $\beta = .05$, and in the first few iterations replace at each step a_n, b_n by a_o, b_o, i.e. iterate only on k with the anticipation that in (38) the expression for k_o is the least accurate. We get

β	.00002	.02	.05
k_0	2	2	2
k_1	1.0193	1.613	1.965
k_2	1.00571	1.319	1.722
k_3	1.00563	1.242	1.566
k_4	1.00563	1.225	1.479
k_5		1.2225	1.445
k_6			1.431
k_7			1.4273

Using the improved values for k, we now continue iterations on a, b and k simultaneously. In the case $\beta = .00002$ there is no point in going on. In the other two cases we get

$\beta = .02$

n	a_n	b_n	k_n
5	$.04 = a_o$	$.0222 = b_o$	1.2225
6	.0407	.0226	1.200
7	.0408	.0226	1.200

$\beta = .05$

n	a_n	b_n	k_n
7	$.1 = a_o$	$.0535 = b_o$	1.427
8	.10473	.0560	1.362
9	.10506	.0562	1.348
10	.10508	.0562	1.338

We thus established that for all x,

(43) $$ax + b \leq yy' \leq k(ax + b).$$

On reintroducing the original variables t and $R(t)$, (43) becomes

(44) $$A + \frac{B}{\sqrt{t}} \leq R\dot{R} \leq k(A + \frac{B}{\sqrt{t}})$$

where

$$A = \frac{a}{2}, \quad B = \frac{b}{2}.$$

Appendix

Comments on theorem 2, Section III.

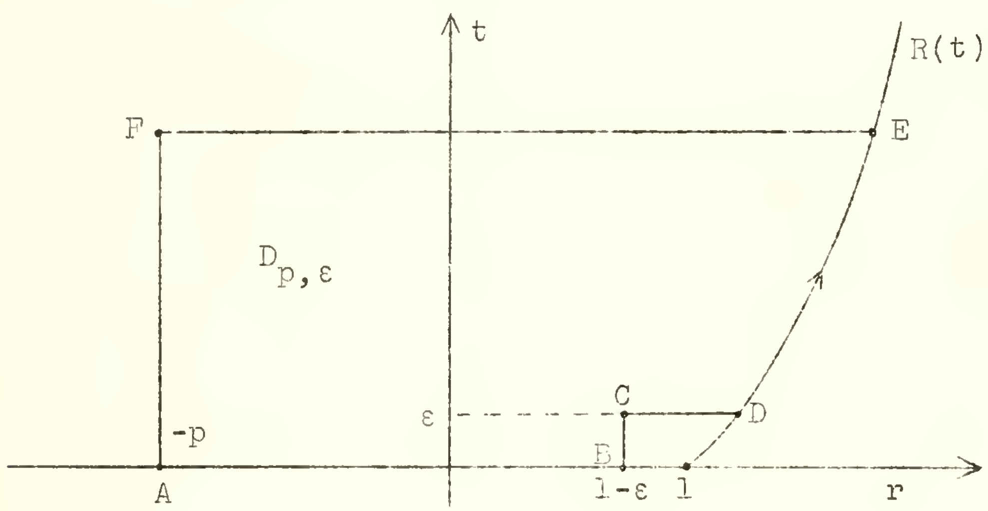
Let $u^\rho(r,t)$ be defined by equation (14) and let $\overline{R}$ be the solution of equation (19). We assert (theorem 2) that

$$u^R(r,t) \equiv 0 \quad \text{for} \quad r < R(t).$$

To prove the theorem we use the well known identity for solutions u of the heat equation

$$2\iint_D (u_r)^2 dr\, dt = \oint_C u^2 dr + 2uu_r dt$$

(see, e.g. [4]), which we apply to u^R in the domain bounded by the curve ABCDEFA. It is assumed that the following



properties of $R(t)$ are known:

$$\mathring{R} > 0, \quad |\dot{R}| \leq \frac{A}{\sqrt{t}}.$$

As to u^ρ (or u^R), the following properties are used

1) u^ρ is a regular solution of the heat equation in $D_{p,\varepsilon}$

2) $u^\rho = 0$, for $t = 0$, except at $r = 1$

3) u^ρ, $u^\rho_r \longrightarrow 0$ as $r \longrightarrow -\infty$

4) $|u^\rho| \leq A$, $|u^\rho_r| \leq \frac{A}{\sqrt{t}}$ near $r = 1$, $t = 0$.

Contributions along various segments of the boundary to the contour integral are:

Along AB $\quad \int_{-p}^{1-\varepsilon} u^2(r,0)dr = 0$

Along BC $\quad |\int_0^\varepsilon 2uu_r dt| \leq 2A^2\sqrt{\varepsilon}$

Along CD $\quad |\int_{1-\varepsilon}^{R(\varepsilon)} u^2(r,\varepsilon)dr| \leq A(2A\sqrt{\varepsilon} + \varepsilon)$,

since $R(\varepsilon) \leq 1 + 2A\sqrt{\varepsilon}$.

Along DE $\quad \int_\varepsilon^t u(R,t)(\dot{R}u(R,t) + u_r(R,t))dt = 0$,

since R satisfies equation (19)

Along EF $\quad -\int_{-p}^{R(t)} u^2(r,t)dr \leq 0$

Along FA $\quad -\int_0^t u(-p,t)u_r(-p,t)dt \longrightarrow 0$ as $p \longrightarrow \infty$.

If we now let $\varepsilon \longrightarrow 0$, and $p \longrightarrow \infty$, we get

$$0 \leq 2\iint_D u_r^2 \, dr\, dt = -\int_{-\infty}^{R(t)} u^2(r,t)dr \leq 0,$$

implying that $\int_{-\infty}^{R(t)} u^2(r,t)dr = 0$, or that $u(r,t) \equiv 0$ in D.

If R were defined by equation (17), then all we would know is that $u_r(R,t) = 0$. The contribution along DE would

be not zero but

$$\int_{\varepsilon}^{t} \dot{R}\, u^2(R,t)dt \geq 0, \qquad \text{since} \quad \dot{R} > 0$$

and we would be in doubt about the sign of the line integral. In case of evaporation, $\dot{R} < 0$, making the last integral non-positive, so that in that case the proof goes through if R satisfies equation (17).

One is tempted to define R by equation (17) and to try to prove first that $u_r(r,t) \equiv 0$ in D. (It would then follow that $u \equiv f(t)$ and consequently that $u \equiv 0$). u_r also satisfies the heat equation, and one has therefore, the identity

$$2\iint_D (u_{rr})^2 dr\, dt = \oint_C u_r^2\, dr + 2u_r u_{rr} dt.$$

The troublesome contribution along DE would now vanish if $u_r(R,t) = 0$, but since u_{rr} is more singular than u_r near $r = 1$, $t = 0$, the contributions along segments BC and CD would not vanish as $\varepsilon \longrightarrow 0$, thus again defeating our attempt.

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Date Due

NOV 7 '60			
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MAY 9 '61			
12/3/62			
	PRINTED	IN U. S. A.	